# Section 4
# Data Quality Review

This section presents the summarized results of QA procedures established to ensure the validity of the zinc and acute toxicity data collected during the demonstration. Section 4.1 discusses zinc data quality, and Section 4.2 discusses acute toxicity data quality. A comprehensive discussion for both zinc and acute toxicity, along with supporting summary tables, is presented in the Technical Evaluation Report.

## 4.1 Zinc Data Quality Review

This section discusses the results of the QA procedures established to ensure the validity of the zinc data collected during the demonstration. The QA procedures were established prior to the demonstration and were recorded in the quality assurance project plan (QAPP) as part of the demonstration plan. Both field and analytical QA procedures were specified to ensure sample integrity and the generation of data of known quality.

### *4.1.1 Quality Assurance Results for Field Sampling Activities*

The procedures followed during field activities to maintain sample integrity and quality are discussed below. They include specifications for sample collection, labeling, containerization, preservation, holding times, and chain of custody.

**Sample Containerization, Preservation, and Holding Times**

This section describes sample labeling, shipment, chain-of-custody, and laboratory receipt procedures for zinc samples. Conformance with and documentation of these procedures provide a definitive record of sample integrity from origin to analysis.

Each sample container was labeled with a unique sample identification number. The label identified the sampling location, date, time of collection, and analysis to be performed. All chain-of-custody forms included the project number, project name, sampler's name, station number, date, time, sampling location, number of containers, and analytical parameters. Samples were hand-delivered to Quanterra Environmental Services in Arvada, Colorado. Chain-of-custody forms gathered during the demonstration were reviewed for content and completeness and appeared in good order.

All samples analyzed for critical parameters arrived at the laboratory intact. Several of the coolers used for shipping the samples arrived with inside temperatures greater than 4 degrees Celsius as specified in the QAPP. However, the results of associated QA samples suggest that the elevated temperature did not affect sample integrity. All samples were analyzed within their designated holding times (6 months); the majority were analyzed within 1 month of sample collection.

**Equipment and Field Blanks**

Equipment blanks were collected during the demonstration to assess sample contamination resulting from sampling equipment. Throughout the demonstration, dedicated sampling equipment was used for sample collection to reduce sample cross contamination. As a result, few equipment blanks or field blanks were collected during the demonstration. The data quality objective (DQO) for equipment and field blanks was results below reporting limits for all analytes.

Two equipment blanks (WEV090794EB and EB012197) were collected with a polyethelene dipper by pouring deionized water into the dipper and decanting the water into an appropriate sample container. The equipment blank collected in September 1994, contained an estimated zinc concentration of 0.019 mg/L, which is below the 0.020 mg/L reporting limit. The equipment blank collected in January 1997, contained 0.052 mg/L zinc, above the 0.020 mg/L reporting limit.

Field blanks were used to assess whether zinc contamination was introduced during the handling, presentation, or transport of aqueous samples. The field blank was prepared by adding deionized water into an appropriate sample container in place of a real sample.

One field blank was collected during the demonstration (FB060194). Zinc was found in this field blank at a concentration of 0.034 mg/L, slightly above the reporting limit of 0.020 mg/L.

The level of contamination in the equipment and field blanks qualifies data near the reporting limit for accuracy. The source of the contamination is unknown; however, the commercial distilled water is suspected. All of the CWS performance data contained zinc concentrations at least one order of magnitude greater than the reporting limit and in most cases two or three orders of magnitude above the reporting limit. Consequently, the demonstration zinc data are considered acceptable for their intended use.

**Method Blanks**

Method blanks verify that laboratory extraction and sample cleanup and concentration procedures used do not introduce contaminants that compromise the analytical results. Method blanks were prepared and analyzed with each batch of laboratory analysis. The method blank DQO was for results to be below reporting limits for all analytes of interest.

Five out of the 40 batches analyzed during this demonstration contained reportable quantities of zinc in the method blanks. Values ranged from 0.020 mg/L to 0.046 mg/L. All samples corresponding to these five analytical batches were qualified for blank contamination (B). All of the sample results were greater than five times the associated blank contamination; thus, no zinc results were qualified as nondetected due to blank contamination (UB).

### *4.1.2 Quality Assurance Results for Sample Analysis*

Analytical QA includes methods and procedures used to ensure data reliability. This process involves establishing data quality objectives for the project data and developing data quality indicators (quanitative or qualitative measures of precision, accuracy, completeness, representativeness, and comparability) that can be used to determine whether the data meet the project's QA objectives.

The QA objective for the CWS demonstration data were established in the QAPP with specific performance goals for precision, accuracy, representativeness, completeness, and comparability. The following sections evaluate the demonstration data with respect to these performance goals.

**Precision and Accuracy**

Precision is a measure of the reproducibility of measurements under a given set of conditions. Accuracy is the degree of agreement between an analytical measurement and the true value. The overall precision for zinc concentrations was a function of both sampling and laboratory precision. Overall precision was evaluated using data from field duplicates, and laboratory precision was evaluated using data from laboratory duplicates. Relative percent difference (RPD) between duplicate samples was used to evaluate precision using the following formula:

$$RPD = \frac{|(A - B)|}{0.5\ (A + B)} \quad X\ 100$$

where: A = first duplicate concentration
B = second duplicate concentration or

Fifteen field duplicate samples were collected during this demonstration, yielding RPDs ranging from 0 to 3.7 percent. Laboratory duplicate control sampling were analyzed for 51 rounds of sampling activities. All laboratory RPDs were within the established DQO of 20 percent with the exception of one, of 28 percent. Overall, the precision objectives for zinc analyses were achieved.

The accuracy of a measurement is affected by errors introduced through the sampling process and in handling, sample matrix, sample preservation, and analytical techniques. A program of sample spiking at the laboratory and analysis of standard reference materials (SRMs) was also used to evaluate laboratory accuracy.

Accuracy for zinc measurements was estimated as percent recovery (%R) of the true analyte level from SRMs and by evaluation of matrix spike (MS) recoveries. The following formula was used to calculate MS percent recovery:

$$\% R = (S-C)/T\ X\ 100$$

where: S = measured spike concentration
C = sample concentration
T = true or actual concentration of the spike or

MS spiking recoveries were all within the DQO limits with one exception. One MS sample analyzed (collected on July 27, 1994) yielded a recovery of 134 percent, slightly above the DQO. When the data were rechecked by the laboratory, the deviations were not found to bias the results sufficiently to affect data use. The laboratory concluded that the magnitude of the errors was too small relative to the zinc concentrations to have a significant effect on the zinc values.

Reported results for the SRM indicate that the analytical method measured larger concentrations of zinc than reported in National Institutes of Standards and Testing (NIST) standard reference material 1643c. The higher recoveries were considered to be the result of matrix interferences and the low level of zinc in the SRM. The DQO for accuracy is 75 to 125 percent recovery. SRM recoveries were 123 and 149 percent. Quanterra was immediately notified of the problem, and the laboratory control samples were checked to confirm that all other analytical controls were within acceptable parameters. Tetra Tech determined that some demonstration results with very low levels of zinc may be positively biased. The zinc results affected are from the upflow cell effluent during the first 6 months of operation.

Overall laboratory accuracy for the demonstration data was acceptable.

**Representativeness**

Representativeness expresses the degree to which sample data accurately and precisely represent the characteristics of a population, parameter variations at a sampling point, or an environmental condition they are intended to represent. For the CWS demonstration, the low RPDs associated with field duplicate results suggest the data collected are representative of the CWS system for the environmental and physical conditions at the Burleigh Tunnel site.

**Completeness**

Completeness is a measure of the amount of acceptable data obtained compared to the amount of data needed to achieve a particular level of confidence in the results. Acceptable data are obtained when (1) samples are collected and analyzed in accordance with the QC procedures outlined in the demonstration plan, and (2) criteria that affect data quality are not exceeded. CWS percent project completeness (%C) was calculated using the following equation:

$$\%C = (V/T) \times 100$$

where: %C = percent completeness
V = number of measurements judged acceptable
T = total number of measurements planned

The QA objective for degree of completeness was 90 percent for the critical parameter zinc. All data collected are considered usable for the intended purpose; therefore, the QA objective for completeness was achieved.

**Comparability**

The comparability parameter is designed to identify deviations in the data that may result from inconsistencies in field conditions, sampling methods, or laboratory analysis. During this demonstration, changes in sampling techniques and laboratory analysis were minimized to ensure comparability of results. However, the end of the first SITE contract and delays in restarting the new SITE contract required the use of data collected by CDPHE. The results of a laboratory intercalibration exercise with Quanterra, the CDPHE laboratory (Analytica), and a referee laboratory suggest that the data are comparable.

## 4.2 Acute Toxicity Data Quality Review

This section discusses the results of QA data collected to document the validity of the acute toxicity data. The QA procedures were established prior to the demonstration and recorded in the QAPP as part of the demonstration plan. Both field and analytical QA procedures were specified to ensure sample integrity and the generation of data of known quality.

### *4.2.1 Analytical Quality Assurance*

Analytical QA is the process of ensuring and confirming data reliability. This process includes establishing DQOs for the project data and developing data quality indicators (quantitative or qualitative measures of precision, accuracy, completeness, representativeness, and comparability) that can be used to evaluate whether the data met the project's QA objectives. The QA objectives for acute toxicity testing during the CWS demonstration

were established in the QAPP and are summarized in the following discussions.

**Water Chemistry Results for Environmental Samples and Reference Toxicant Tests**

To ensure that laboratory water quality conditions did not adversely affect the reference toxicant or environmental sample results, water quality parameters were documented throughout all test series. The water chemistry results indicate that the water quality conditions for testing were appropriate for the test organisms during all test dates and that no abnormal water conditions were documented that could influence the survivability results.

**Precision and Accuracy**

Precision and accuracy in toxicity tests are controlled and evaluated through documentation of reference toxicant responses of indicator species against inter- and intra-laboratory historical records; and by carefully controlling and documenting the environmental conditions tested. The following discussion documents the laboratory testing conditions for growth, feeding, and maintenance of indicator species during the tests; and documents the results of indicator species survivability results against laboratory historical records for identical tests.

Acute toxicity and metal concentration in the mine drainage were used to infer a response relationship between the most prevalent toxic component present (zinc) and indicator species survival. Preliminary chemical analysis had identified zinc in various forms as the most predominant metal contaminant.

Zinc sulfate was used as a reference toxicant to simulate the population response of the indicator species to a soluble zinc compound present in the mine drainage matrix. Potassium chloride was used as a laboratory reference test for population viability and toxic response of the indicator species.

Pimephales promelus and Ceriodaphnia dubia were used as the test organism populations in the 48-hour static-renewal acute toxicity tests. Indicator species survival rates (LC50) at the 95 percent confidence level (EPA 1993a) in a static series of potassium chloride and zinc sulfate concentration dilutions were calculated and compared with laboratory historical records. The comparison provided a control on the viability of the test species and the testing methodology.

The quantitative precision and accuracy requirements for acute toxicity for Pimephales promelus and Ceriodaphnia dubia when exposed to zinc sulfate were established by toxicant equivalent concentration values generated from both external and internal laboratory records of earlier tests. The quantitative precision and accuracy objectives for acute toxicity for Pimephales promelus and Ceriodaphnia dubia when exposed to potassium chloride were established by monthly cumulative laboratory toxicant equivalent concentration values.

All reference toxicant results fell within the prescribed ranges, indicating that the response of the indicator species response to test conditions was appropriate for evaluating the toxin present. Therefore, the quantitative results of acute toxicity to the environmental samples are comparable to other tests under identical conditions.

**Sample Duplicates**

The results of sample (field) duplicates is another indicator of overall precision. The sample duplicate was collected on February 27, 1995 from the treated effluent from the downflow cell (samples designated WED and WEDII).

Generally, the analysis of duplicate acute toxicity values for sampling and analytical precision is a numerical comparison of the difference in reported acute toxicity values to the magnitude of the values themselves. However, sample WED for February 27, 1995 was not toxic enough to generate an LC50 value, which is the normal endpoint for acute toxicity analysis. Consequently, the analysis of test sampling and analytical precision presented is a subjective comparison of the sample and duplicate routine chemistry and intermediate toxicity results.

The chemistry for duplicate samples WED and WEDII shows no significant difference, with less than 10 percent variation in all measured parameters. Those variables having the greatest difference – in pH, DO, and temperature – were consistently lower for WEDII than for WED. The values, however, do not strongly indicate a difference in water quality conditions. The initial and final chemistry for both species tests also show slight differences, but no consistent variability in an individual parameter.

Qualitatively, the survival rates for C. dubia of the individual sample dilutions for duplicate samples WED and WEDII both show very slight toxicity, especially noting that both controls had survival rates of 20/20. Quantitatively, the 100 percent WEDII sample yields a survival ratio

statistically different than the control when tested with Steel's Many-One-Rank test at an = 0.05 (EPA 1993a). WED at 100 percent concentration did not exhibit sufficient mortality for the survival ratio to be statistically different than the control.

The acute tests with P. promelas do not show any statistical difference from the control for WED or for WEDII; therefore, no toxicity for this species is evident. In general, C. dubia is more sensitive to environmental toxicants, so the absence of toxicity for P. promelas supports the presumption that WEDII is slightly toxic. Using the C. dubia results alone, it appears that there is a slight difference in the acute toxicity of the duplicate samples (WED and WEDII). Also, the arrival, initial, and final chemistry data show a difference in the characteristics in the ambient water between the two samples. Therefore, the duplicate analysis indicates that there is sufficient variability in the effluent stream to reflect a difference in the toxicity results of duplicate samples. However, this difference between duplicates is sufficiently small that the results of the acute toxicity tests, with LC50 as the endpoint, are not sensitive enough to calculate a coefficient of variation for effluent mine drainage samples.

**Representativeness**

For this project, representativeness for acute toxicity tests involved sample size, sampling times relative to seasonal temperature variation, and sampling locations. Most importantly, the changes due to seasonal environmental conditions needed to be documented to enable evaluation of zinc concentration reduction by biological conversion and uptake during cold stress conditions against warm temperature conditions. The QA goal was to obtain samples that represented biological water quality, measured by acute toxicity, in the treated and untreated mine drainage under typical seasonal environmental conditions. The primary seasonal environmental parameter of concern was temperature due to the regional extremes present at the demonstration location.

Prior to the demonstration, it was known that three or four seasonal cycles would be required to conduct a statistical analysis of seasonal variation. The project budget and time schedule did not permit this type of data collection; consequently, the QA goal for representativeness was limited to successfully collecting data that would enable a limited evaluation of seasonal rise and fall of acute toxicity values in response to seasonal temperature stress. Since acute toxicity and zinc concentration data were obtained under environmental conditions representative of seasonal fluctuations in temperature in mine drainage influent and effluent, the QA objective for representativeness was met.

**Completeness**

Completeness is an assessment of the amount of valid data obtained from a measurement system compared to the amount of data expected to achieve a predefined quantity of information or level of confidence. The percent completeness is calculated by dividing the number of samples with acceptable data by the total number of samples planned to be collected and multiplying the result by 100. Greater than 90 percent completeness was achieved for all demonstration samples, and 100 percent of the critical samples for acute toxicity achieved acceptable results.

**Comparability**

The acute toxicity tests were conducted in accordance with the EPA guidance document "Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms" (EPA 1991). All quality assurance guidance procedures have been adhered to, and the quantitative results for all QA criteria for reference toxicity fall within the specified limits. Therefore, the demonstration data are considered comparable to other acute toxicity data generated using these standard methods and adhering to the QA guidelines.

## 4.3 Noncritical Parameters Data Quality Review

Data quality review for the first noncrtical objective of substrate utilization, and the third noncritical objective of effluent impact to Clear Creek were included in the review for the number one critical objective data. Analytical results for these two noncritical parameters were within the quality assurance objectives stated in the Demonstration Plan (PRC 1995).

Data quality results for noncritical objective number two, the metal removal by sulfate-reducing bacteria were within the parameters cited in the Demonstration Plan. As stated in the plan, the evaluation of sulfate-reduction was expected to be more qualitative in nature. Results for the bacteria counts and acid-volatile sulfides are considered acceptable quality.

Specific data quality assurance objectives for the fourth, and final noncritical ojbective, compiled capital and

operating costs, were not stated in the Demonstration Plan. However, cost tracking and compilation was performed using a best professional judgment approach. These data are considered accurate and usable within accepted professional standards.